

## CLAIMS

1. An acid copper plating solution comprising copper ions, an organic acid or an inorganic acid, chloride ions, high molecular weight surfactant which controls the electrodeposition reaction, and a sulfur-containing saturated organic compound which promotes the electrocoating rate, wherein the high molecular weight surfactant comprises at least two types with different hydrophobicities.

2. The acid copper plating solution according to claim 1, wherein all of the at least two types of high molecular weight surfactants with different hydrophobicities are nonionic surfactants and the concentration of a surfactant having comparatively strong hydrophobicity is less than the concentration of a surfactant having comparatively weak hydrophobicity.

3. The acid copper plating solution according to claim 1, wherein among the at least two types of high molecular weight surfactants with different hydrophobicities, the concentration of a nonionic surfactant having comparatively strong hydrophobicity is equal to or less than the critical micelle concentration in the acid copper plating solution.

4. The acid copper plating solution according to claim 1, wherein among the at least two types of high molecular weight

surfactants with different hydrophobicities, the concentration of a nonionic surfactant having comparatively weak hydrophobicity is equal to or more than the critical micelle concentration in the acid copper plating solution.

5

5. The acid copper plating solution according to claim 1, wherein among the at least two types of high molecular weight surfactants with different hydrophobicities, the concentration of a nonionic surfactant having comparatively strong hydrophobicity is equal to or less than the critical micelle concentration in the acid copper plating solution and the concentration of a nonionic surfactant having comparatively weak hydrophobicity is equal to or more than the critical micelle concentration in the acid copper plating solution.

15

6. The acid copper plating solution according to claim 1, wherein the at least two types of high molecular weight surfactants with different hydrophobicities comprise a nonionic surfactant and a surfactant other than the nonionic surfactant, and the concentration of the nonionic surfactant is higher than the concentration of the surfactant other than the nonionic surfactant.

7. The acid copper plating solution according to claim 1, wherein the at least two types of high molecular weight surfactants with different hydrophobicities comprise a nonionic surfactant and a surfactant other than the nonionic

surfactant, and the surfactant other than the nonionic surfactant is a cationic surfactant, a surfactant which is nonionic but exhibits cationic properties under strong acidic conditions, or an amphoteric surfactant.

5

8. The acid copper plating solution according to claim 1, wherein the at least two types of high molecular weight surfactants with different hydrophobicities comprise a nonionic surfactant and a surfactant other than the nonionic surfactant, and the concentration of the surfactant other than the nonionic surfactant is equal to or lower than the critical micelle concentration.

9. The acid copper plating solution according to claim 1, wherein the at least two types of high molecular weight surfactants with different hydrophobicities comprise a nonionic surfactant and a surfactant other than the nonionic surfactant, and the concentration of the nonionic surfactant is equal to or higher than the critical micelle concentration.

20

10. The acid copper plating solution according to claim 1, wherein the at least two types of high molecular weight surfactants with different hydrophobicities comprise a nonionic surfactant and a surfactant other than the nonionic surfactant, and the concentration of the nonionic surfactant is equal to or higher than the critical micelle concentration and the concentration of the surfactant other than the nonionic

surfactant is equal to or lower than the critical micelle concentration.

11. An electrolytic plating method comprising  
5 performing plating at a cathode current density in the range of 0.1-30 mA/cm<sup>2</sup> using the acid copper plating solution of claim 1.

12. A plating method for forming a plating film on a  
10 conductor layer, which is formed on at least a part of a structural object having a concave-convex pattern on a semiconductor substrate, comprising providing a cathode potential to the conductor layer and supplying a plating solution which electrically connects an anode with the  
15 conductor layer, wherein the plating solution contains 25-75 g/l of copper ion and 0.4 mol/l of an organic acid or inorganic acid and an electric resistor is installed between the conductor layer and the anode.

20 13. The plating method according to claim 12, carried out at an electrical conductivity of 3 S/m or less.

14. The plating method according to claim 12, wherein the organic acid or inorganic acid is sulfuric acid, alkane  
25 sulfonic acid, or alkanol sulfonic acid.

15. The plating method according to claim 12, wherein

a copper compound selected from the group consisting of copper sulfate, copper oxide, copper chloride, copper carbonate, copper pyrophosphate, copper alkane sulfonate, copper alkanol sulfonate, and organic acid copper is used as a copper ion source.

16. The plating method according to claim 12, wherein the organic acid or inorganic acid is sulfuric acid and the copper ion source is copper sulfate.

17. The plating method according to claim 12, wherein the organic acid or inorganic acid is sulfuric acid, the copper ion source is copper sulfate, and the copper ion concentration is 58 g/l or less.

18. The plating method according to claim 12, wherein the concave-convex pattern formed on a semiconductor substrate comprises a pattern with a wiring width or via of 0.1  $\mu\text{m}$  or less.

19. A plating method for forming a wiring circuit on an electronic circuit substrate having fine holes and trenches, comprising forming a plating film on a conductor layer, which is formed on at least a part of the substrate, and filling the holes and trenches with copper, wherein the plating film is formed by using an acid copper plating solution containing copper ions, organic or inorganic acid, chloride ions, sulfur-containing saturated organic compound, and high

molecular weight surfactant controlling electrocoating at a concentration of 500 ppm or more.

20. The plating method according to claim 19, wherein  
5 a cathode potential is applied to a conductor layer when the electronic circuit substrate on which the conductor layer has been formed is put into the plating bath.

21. The plating method according to claim 20, wherein  
10 a cathode potential is applied at a constant current or constant voltage to a conductor layer when the electronic circuit substrate on which the conductor layer has been formed is put into the plating bath.

15 22. The plating method according to claim 19, wherein the fine holes and trenches formed on an electronic circuit substrate comprise a copper seed layer with a thickness of 1-100 nm, the holes and trenches having an opening width of 1  $\mu$ m or less and an aspect ratio of 5 or more.

20

23. A plating method comprising producing a plating film with a thickness of 10-100 nm on a conductive layer which is formed on at least a part of an electronic circuit substrate having fine holes and trenches using an acid copper plating  
25 solution containing copper ions, organic or inorganic acid, chloride ions, sulfur-containing saturated organic compound, and high molecular weight surfactant controlling

electrocoating at a concentration of 500 ppm or more, and further plating until the fine holes and trenches are filled with copper using an acid copper plating solution containing copper ions, organic or inorganic acid, chloride ions,  
5 sulfur-containing saturated organic compound, and high molecular weight surfactant controlling electrocoating at a concentration of 10-100 ppm.

24. The plating method according to claim 23, wherein  
10 the fine holes and trenches formed on an electronic circuit substrate comprise a copper seed layer with a thickness of 1-100 nm, the holes and trenches having an opening width of 1  $\mu\text{m}$  or less and an aspect ratio of 5 or more.

15